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Bipyrrolidine salan alkoxide complexes of lanthanides: synthesis, characterisation, activity in the polymerisation of lactide and mechanistic investigation by DOSY NMR

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Four dimeric lanthanide alkoxide complexes bearing ONNO bipyrrolidine salan ligands ($L^{Me}H_2/L^{tBu}H_2$) have been prepared with Nd, Sm and Yb. Depending on the metal and substituents, these complexes adopt varying coordination geometries. While investigating the hydrolytic degradation of these complexes, three dimeric mixed alkoxide/hydroxide and bis-hydroxide products were also prepared, isolated and characterised. Despite paramagnetism, 1H NMR and Diffusion ordered spectroscopy (DOSY) allowed additional characterisation alongside that of elemental and single-crystal X-ray diffraction analyses. These systems were very active for the controlled ring-opening polymerisation (ROP) of *rac*-lactide (LA), in industrially relevant melt conditions and in solution, yielding complete conversion within 5 minutes at $[Ln]:[LA]$ ratios up to 3000:1 in toluene, 80 °C, whilst retaining low dispersities ($\bar{D} = 1.1$). 1H DOSY NMR spectroscopy was employed to monitor polymer growth from the metal centres *in situ*, and revealed a dinuclear catalytic active species.

Introduction

With the dependence on fossil fuels resources and the environmental persistence of most commodity polymers, our societal reliance on plastics is now unanimously viewed as unsustainable.¹ Supported by public opinion, this has triggered a concerted research effort between academia and industry towards the development of sustainable alternatives from renewable resources.^{2–5} Polylactide (PLA), a thermoplastic aliphatic polyester derived from lactic acid, is arguably one of the most widely studied degradable and renewable polymer. PLA is commercially available for packaging and fibre applications,⁶ and prepared through solvent-free ring-opening polymerisation (ROP) of lactide (LA). LA can be utilised as either the enantiomerically pure L-LA, or as a racemic mixture of D and L monomers (*rac*-LA), the latter allowing atactic, heterotactic or isotactic microstructures. This is important as the physical properties of the polymer are intrinsically linked to the polymer microstructure, with atactic and heterotactic PLA being amorphous, and heterotactic PLA having a slightly lower T_g (~50 vs. 45 °C).^{7,8} Isotactic PLA is the most sought after structure as it can form a crystalline stereocomplex with a melting temperature ($T_m = 230$ °C) enhanced compared to individual crystalline PLLA or PDLA ($T_m = 180$ °C).⁸ Over the past decades, the drive to achieve isotactic PLA from *rac*-LA, for applications requiring enhanced thermal and mechanical properties, prompted the development of a wide range of organocatalysts and metal complexes for the controlled and stereoselective ROP

of lactide.^{2,7,9–11} Indeed, many studies have shown that PLA microstructure can be controlled by judicious choice of metal centre and ligand(s). However, despite much effort, including some computational studies,^{12–15} challenges still remain to fully understand the interplay between metal, ligand, monomer and the growing polymer chain. There remains a high degree of serendipity in the stereochemical outcome of the polymerisation, with unpredictable tacticities achieved from metal-ligand combinations.

It is noteworthy that while subtle changes in ligands have been extensively shown to induce change in stereoselectivity,^{16–20} systematic studies across a range of metals (period or series) are less common. Several examples have however shown that the metal can significantly influence the outcome of the polymerisation.^{21,22} Changes in selectivity have thus been observed by Williams and co-workers for phosphasalen lanthanide complexes (going from heteroselective to isoselective when going from La to Lu),²³ and by Ma and co-workers for a series aminophenolate Zn(II)/Mg(II) complexes (from heteroselectivity with Zn to isoselectivity with Mg).²⁴ We have ourselves demonstrated that a bipyrrolidine salan ligand $L^{Me}H_2$ can lead to isotactic PLA when coordinated to Zr and Hf, atactic PLA with Ti and heterotactic PLA with Al.^{25,26} Increasing the steric bulk with $L^{tBu}H_2$ removed any selectivity when complexed to Al, but heterotactic PLA was seen with In.²⁷

Herein, we report the synthesis of a series of lanthanide (Nd, Sm, Yb) alkoxide complexes bearing these bipyrrolidine salan ligands, their characterisation and their activity in the polymerisation of *rac*-LA. While no change in stereoselectivity was observed and synthetic challenges limited the extent of our study, we have used 1H diffusion ordered NMR spectroscopy (1H DOSY NMR) to monitor polymer growth from the metal centres *in situ*, which also revealed a dinuclear active species.

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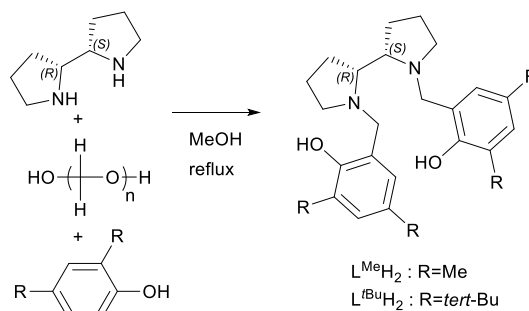
*Electronic Supplementary Information (ESI) available: 1H and $^{13}C\{^1H\}$ NMR spectra of $[L^{Me}Sm(OiPr)_2]$ and $[L^{Me}Sm(OH)_2]$; single-crystal X-ray diffraction data for all complexes (CCDC reference numbers 1844088–1844094); polymerisation kinetic data; DOSY NMR data; plots of M_n and \bar{D} vs. conversion; SEC traces and MALDI-ToF mass spectra of polymers. See DOI: 10.1039/x0xx00000x

Results and discussion

Complex synthesis

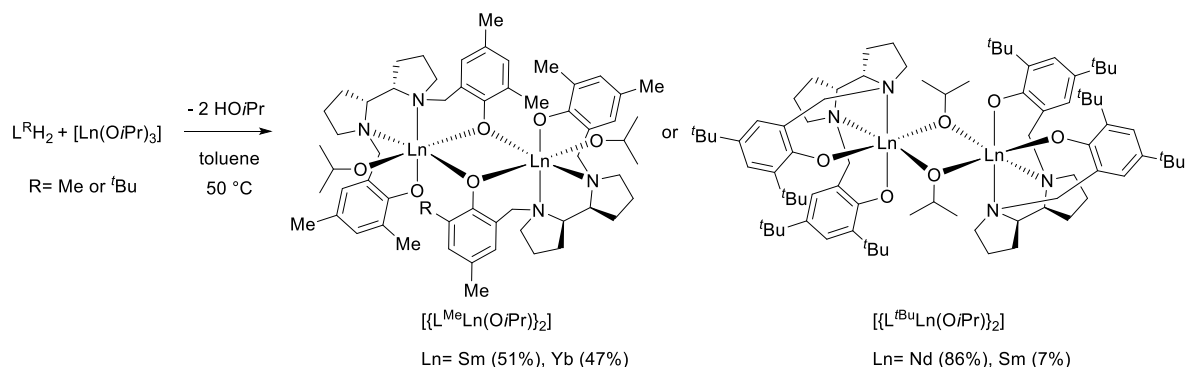
Salan ligands $L^{\text{Me}}\text{H}_2$ and $L^{\text{tBu}}\text{H}_2$ were synthesised from *meso*-2,2'-bispyrrolidine via a Mannich reaction, as previously reported.²⁵ $L^{\text{Me}}\text{H}_2$ and $L^{\text{tBu}}\text{H}_2$ feature methyl and *tert*-butyl substituents at the 2- and 4- positions of the phenol rings, respectively (Scheme 1). Metal coordination was then achieved by reaction of the ligands with commercial lanthanide isopropoxide precursors ($[\text{Ln}(\text{O}i\text{Pr})_3]$, Ln: Nd, Sm, Yb), in anhydrous toluene at 50 °C for 3 hours, under an Ar atmosphere (see experimental section for details). While all possible ligand/metal combinations were attempted, only $[\{L^{\text{Me}}\text{Yb}(\text{O}i\text{Pr})\}_2]$, $[\{L^{\text{Me}}\text{Sm}(\text{O}i\text{Pr})\}_2]$, $[\{L^{\text{tBu}}\text{Sm}(\text{O}i\text{Pr})\}_2]$, $[\{L^{\text{tBu}}\text{Nd}(\text{O}i\text{Pr})\}_2]$ dialkoxide species could be isolated as crystals, with poor to very good yields (47, 51, 7 and 86% yield, respectively).

These complexes were all characterised by elemental analysis and single crystal X-ray diffraction which are in agreement with the expected products (Scheme 2). Despite its paramagnetism, $[\text{L}^{\text{Me}}\text{Sm}(\text{O}i\text{Pr})_2]$ could also be characterised by ^1H NMR (Figure S1). Anisotropic shifting proved more severe for Nd and Yb systems, yielding significant line broadening, large increase in spectral width and a lower signal-to-noise ratio.²⁸ Nevertheless, some clarity was seen for $[\text{L}^{\text{Me}}\text{Yb}(\text{O}i\text{Pr})_2]$, aiding identification in the solution state and assisting during hydrolytic degradation studies (Figure S8 and *vide infra*).



Scheme 1 Synthesis of *meso* ligands $L^{\text{Me}}\text{H}_2$ and $L^{\text{tBu}}\text{H}_2$.

X-ray diffraction analysis revealed the influence of the ligand on the coordination pattern of the metals (Scheme 2, Figure 1). All complexes proved to be dimeric in the solid state, with centrosymmetric structures containing two Ln centres connected to each other by two bridging $\mu\text{-O}$ atoms, the centre of inversion sitting in the middle of the Ln_2O_2 quadrangle. However, the methyl-substituted ligand favoured the bridging of the metals by the phenoxide moiety of the ligand, whereas the *tert*-butyl-substituted ligand led to bridging *isopropoxide* moieties, contrasting with a *tert*-butyl tripodal bisphenolate Sm system published by Mountford and coworkers.¹³ Figure 1 illustrates the molecular structure of representative complexes $[\{L^{\text{Me}}\text{Yb}(\text{O}i\text{Pr})\}_2]$ and $[\{L^{\text{tBu}}\text{Nd}(\text{O}i\text{Pr})\}_2]$, the Sm complexes being their isometric counterparts.



Scheme 2 Synthesis of complexes $[\{L^{\text{Me}}\text{Ln}(\text{O}i\text{Pr})\}_2]$ and $[\{L^{\text{tBu}}\text{Ln}(\text{O}i\text{Pr})\}_2]$.

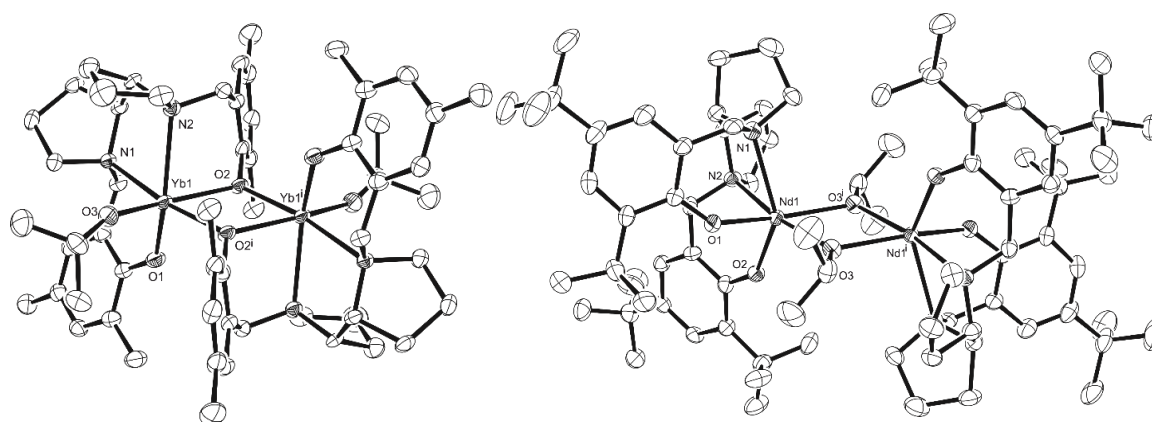


Figure 1 ORTEP-plots (50% thermal ellipsoids) of the molecular structure of complexes $[\{L^{\text{Me}}\text{Yb}(\text{O}i\text{Pr})\}_2]$ (left) and $[\{L^{\text{tBu}}\text{Nd}(\text{O}i\text{Pr})\}_2]$ (right). Hydrogen atoms and residual crystallisation solvent molecules have been omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for solid state structures of complexes $[\{L^{Me}Yb(OiPr)\}_2]$, $[\{L^{Me}Sm(OiPr)\}_2]$, $[\{L^{tBu}Sm(OiPr)\}_2]$ and $[\{L^{tBu}Nd(OiPr)\}_2]$, obtained by single crystal X-ray diffraction analysis

	$[\{L^{Me}Yb(OiPr)\}_2]$	$[\{L^{Me}Sm(OiPr)\}_2]$	$[\{L^{tBu}Sm(OiPr)\}_2]$	$[\{L^{tBu}Nd(OiPr)\}_2]$
Ln1–Ln1 ⁱ	3.6959(4)	3.8599(2)	3.8556(3)	3.8860(6)
Ln1–O1	2.112(3)	2.1902(15)	2.226(2)	2.263(4)
Ln1–O2	2.275(3)	2.3310(14)	2.177(2)	2.179(4)
Ln1–O3	2.035(3)	2.1148(16)	2.340(2)	2.336(4)
Ln1–O _{bridging} ^j	2.254(3)	2.3989(14)	2.342(2)	2.375(4)
Ln1–N1	2.499(4)	2.6095(16)	2.649(3)	2.580(5)
Ln1–N2	2.533(4)	2.6299(16)	2.674(3)	2.765(5)
Ln1–O _{bridging} –Ln1 ⁱ	109.39(11) (O _{bridging} = O2)	109.38(5) (O _{bridging} = O2)	110.85(10) (O _{bridging} = O3)	111.14(15) (O _{bridging} = O3)
O1–Ln1–O2	101.80(12)	102.26(5)	100.27(10)	96.35(15)
O1–Ln1–O3	103.72(14)	105.56(6)	87.95(9)	94.42(14)
O1–Ln1–N1	80.73(12)	78.81(5)	76.11(9)	75.43(15)
O1–Ln1–N2	146.76(12)	141.50(6)	91.98(9)	98.44(15)
N1–Ln1–O2	171.02(11)	168.89(5)	141.27(9)	137.54(15)

Table 1 contains selected bond lengths (Å) and angles (°) for the complexes synthesised, obtained from the X-ray diffraction analysis. Each hexacoordinated Ln atoms exhibits a distorted octahedral geometry (for example, for $[\{L^{tBu}Nd(OiPr)\}_2]$, O1–Nd1–O2 = 96.35(15)°, O1–Nd1–N1 = 75.43(15)°, N2–Nd1–O3 = 166.98(14) and O2–Nd1–N2 = 72.58(15)°, with a β -*cis* conformation of the tetradentate (ONNO) ligand for all complexes, *i.e.* three atoms (O, N and N) occupying equatorial positions whereas one O atom is in axial position. This is analogous to the group 4 complexes previously published.^{25,26} With these geometric features and coordination patterns in mind, it is possible that in the case of Nd, the increased ionic radius compared to Sm (1.109 Å vs. 1.079 Å) prevents formation of $[\{L^{Me}Nd(OiPr)\}_2]$, while in the case of Yb, the decreased ionic radius compared to Sm (0.985 Å vs. 1.079 Å) impedes the formation of $[\{L^{tBu}Yb(OiPr)\}_2]$.

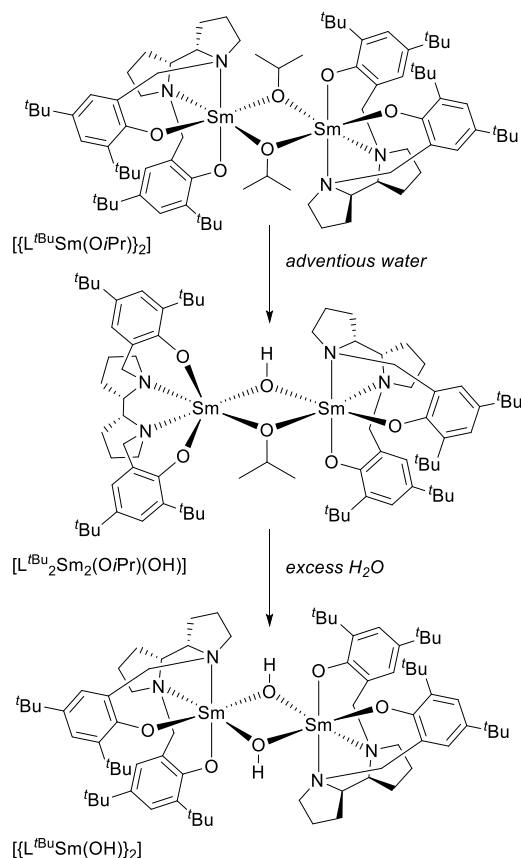
Ln–ONNO–salan–alkoxides are rare in the literature,²⁹ and to the best of our knowledge the examples reported herein represent the first Ln–salan isopropoxide species crystallographically characterised. This is surprising given the commercial availability of the tris(isopropoxide) lanthanide precursors. It is fair to say that the preferred method in the literature for Ln-mediated ROP is to prepare the lanthanide-silylamido complex, as a direct initiator or as a precursor for an alkoxide, formed by addition of exogenous alcohol.^{30–34}

Complex hydrolytic degradation

Recently, Mehrkhodavandi and co-workers showed how a dimeric indium hydroxide species obtained from hydrolytic degradation could be returned into an active initiator for ROP of LA from the addition of excess alcohol.³⁵ Despite hydrolysis

products commonly reported for lanthanide alkoxide complexes, few studies actually isolate and identify such compounds with no examples reported in the context of ROP catalysis. With the potential to gain valuable insight into the degradation mechanism and role of the initiating group in the ROP of lactide, we investigated the hydrolytic degradation of our Ln–OiPr systems.

All the complexes synthesised were highly air and moisture sensitive and had to be manipulated under an inert atmosphere, using dry solvents. In fact, in the case of $[\{L^{tBu}Sm(OiPr)\}_2]$, the desired complex could only be isolated with 7% crystalline yield. From the recrystallisation mother liquor of $[\{L^{tBu}Sm(OiPr)\}_2]$, a second recrystallisation provided 69 % yield of mono-hydroxide species $[L^{tBu}_2Sm_2(OiPr)(OH)]$, which was characterised by X-ray diffraction and elemental analysis, and is likely formed from adventitious moisture. Similarly, isometric $[L^{tBu}_2Yb_2(OiPr)(OH)]$ could also be isolated (see ESI for X-ray diffraction, and experimental section for elemental analysis data and ¹H NMR spectra). Further hydrolysis of $[L^{tBu}_2Sm_2(OiPr)(OH)]$ could be carried out by addition of 10 equivalents of water, and resulted in the isolation of bis-hydroxide dimer $[\{L^{tBu}Sm(OH)\}_2]$, which was characterised by X-ray diffraction and elemental analysis (Scheme 3). Figure 2 presents the molecular structure of Sm complexes $[L^{tBu}_2Sm_2(OiPr)(OH)_2]$ and $[\{L^{tBu}Sm(OH)\}_2]$. Table 2 details some key geometrical parameters of both Sm complexes. While $[\{L^{tBu}Sm(OH)\}_2]$ shows a centrosymmetric dinuclear structure with the two Sm centres bridged by the O atoms of the hydroxide groups, $[L^{tBu}_2Sm_2(OiPr)(OH)]$ features no such symmetry.

Scheme 3 Hydrolytic degradation of $[\{L^{tBu}Sm(OiPr)\}_2]$.

In the case of methyl-substituted ligand, no crystalline products from hydrolytic degradation could be isolated. However, the hydrolysis in air of a solution of $[\{L^{Me}Sm(OiPr)\}_2]$ could be followed by 1H NMR, which showed the progressive formation of *isopropanol* and of $-OH$ groups, with no further evolution after 36 hours (Figure S3-4). DOSY NMR spectroscopy also revealed degradation product(s) to have similar diffusion coefficient to $[\{L^{Me}Sm(OiPr)\}_2]$, and suggested metal complexes of similar size. Collectively, these elements point towards the formation $[L^{Me}_2Sm_2(OiPr)_x(OH)_{2-x}]$ species. It is worth noting that the nature of the metal also influences hydrolysis as for $[\{L^{Me}Yb(OiPr)\}_2]$, complete degradation with release of free protonated ligand was observed after ca. 5 hours (Figure S9).

Complex reactivity with lactide: monitoring by DOSY NMR

Despite their performances in the ROP of cyclic esters, in particular lactide, there are limited reactivity and mechanistic studies in the literature between lanthanide complexes and lactide, as paramagnetism and fast rates make traditional methods unsuitable.³¹ However, such studies have the potential to unravel structure/activity relationships that can guide future catalyst development. Only mild isotropic shifting in the 1H NMR of $[\{L^{Me}Sm(OiPr)\}_2]$ offered the opportunity to study the fundamental reaction of the complex with lactide. While our studies did not isolate any Sm-lactide adduct or a metal complex with a growing lactide chain, we were able to achieve some insight into the reaction using Diffusion Ordered Spectroscopy (DOSY) NMR (see details in ESI). Recently, DOSY has become a powerful tool in polymer science, with new methodologies being developed to accurately estimate the molecular weights for macromolecules.^{36–38}

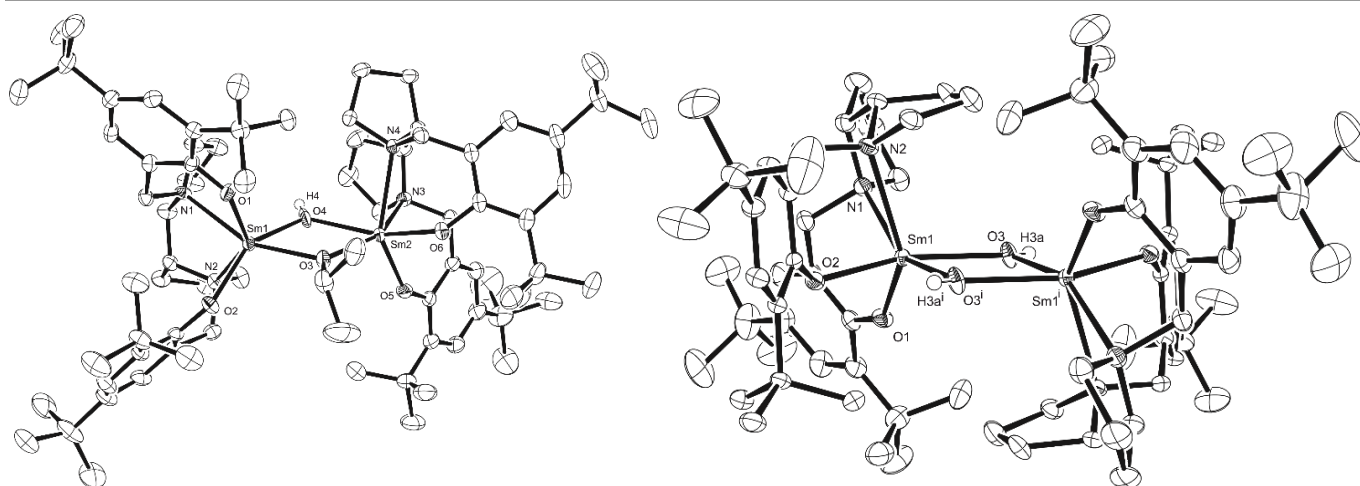


Figure 2 ORTEP-plots (50% thermal ellipsoids) of complexes $[L^{tBu}_2Sm_2(OiPr)(OH)]$ (left) and $[\{L^{tBu}Sm(OH)\}_2]$ (right). Hydrogen atoms, except those bound to O3/O3' and residual crystallisation solvent molecules have been omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for solid state structures of complexes $[L^{tBu}_2Sm_2(OiPr)(OH)]$ and $[(L^{tBu}Sm(OH))_2]$, obtained by single crystal X-ray diffraction analysis.

$[L^{tBu}_2Sm_2(OiPr)(OH)]$		$[(L^{tBu}Sm(OH))_2]$	
Sm1–Sm2	3.8093(2)	Sm1–Sm1 ⁱ	3.8731(2)
Sm1–O1	2.1842(16)	Sm1–O1	2.1852(19)
Sm1–O2	2.1829(17)	Sm1–O2	2.2331(18)
Sm1–O3	2.3189(18)	Sm1–O3	2.1148(16)
Sm1–O4	2.3568(18)	Sm1–O3 ⁱ	2.3068(19)
Sm1–N1	2.639(2)	Sm1–N1	2.606(2)
Sm1–N2	2.633(2)	Sm1–N2	2.621(2)
Sm2–O5	2.1665(17)	Sm1–O3–Sm1 ⁱ	112.18(8)
Sm2–O6	2.2063(18)	O1–Sm1–O2	95.34(7)
Sm2–N3	2.659(2)	O1–Sm1–O3	98.30(7)
Sm2–N4	2.584(2)	O1–Sm1–N1	75.54(7)
Sm2–O3	2.2971(17)	O1–Sm1–N2	140.05(7)
Sm2–O4	2.3930(19)	N1–Sm1–O2	103.22(7)
Sm1–O3–Sm2	111.23(7)	N1–O3–O2–Ln	11.68
Sm1–O4–Sm2	106.64(8)		

The reaction of $[(L^{Me}Sm(OiPr))_2]$ with 2 equivalents of *rac*-lactide (one per metal) was monitored by 1H DOSY NMR at 25 °C in $CDCl_3$ in an attempt to mimic ROP conditions whilst limiting convection issues from high temperature diffusion measurements.³⁹ The dimeric structure of the complex was shown to be retained, with only a slight decrease in diffusion coefficient (Table 3, entry 2 vs. entry 1). Furthermore, this main species combined signals of coordinated ligand L^{Me} , metal-bound *isopropoxide*, lactide, and an *isopropyl* lactate species (Figure S11).^{40,41} This suggests a Sm dimer species, with a lactate chain growing from one metal centre, and a lactide coordinated to a metal centre (same metal or different). This is also supported by the evaluation of the molecular weight of this species, using the method derived by Morris and co-workers (Table 3, entry 2).^{42,43}

By increasing the amount of lactide to 20 equivalents, further polymerisation could be monitored by DOSY (Figure 3), with no evidence of any changes in the active species. The molecular weight derived by diffusion coefficients was further-

-more aligned with the expected one (Table 3, entry 3). Exposing the reaction mixture to air to quench the polymerisation led to an increase in diffusion coefficient of the polymer resonances, consistent with cleavage of the growing polymer chain(s) from the dimer (Table 3, entry 4). The polymer was next isolated and analysed by SEC, giving M_n values consistent with those determined via DOSY (Figure S26), and giving clear indication of only one polymer chain growing from the dimer.

Based on these observations, under these conditions, the catalytic active species is dinuclear, and more work is needed to establish if the presence of a second metal is advantageous or not. A cooperative mechanism could open the way to more efficient heterodinuclear metal complexes based on this ligand framework. Such effect has been previously predicted by DFT calculations then observed experimentally in the related ring-opening copolymerisation of epoxides and CO_2 .^{44,45}

Table 3 Reactivity of $[(L^{Me}Sm(OiPr))_2]$ with *rac*-LA, followed by DOSY NMR spectroscopy^a

Entry	<i>rac</i> -LA equiv.	D^c $10^{-9} m^2 s^{-1}$	$D_{solvent}^e$ $10^{-9} m^2 s^{-1}$	DOSY M_n^f $g mol^{-1}$	Theo. M_n^g $g mol^{-1}$	SEC M_n^i $g mol^{-1}$
1	-	0.589	1.77	1269	1236	-
2 ^b	2	0.569	1.93	1371	1380	-
3 ^c	20	0.357	1.99	4091	3830	-
4 ^{c,d}	20	0.427	1.97	2668	2584 ^h	2800

^a 1H NMR diffusion ordered spectroscopy (DOSY) studies of $[(L^{Me}Sm(OiPr))_2]$ in $CDCl_3$ (1 mL), $[I] = 2.4 mmol L^{-1}$. ^b $[I] = 2.4 mmol L^{-1}$, $[rac-LA] = 4.8 mmol L^{-1}$, reaction left at 25 °C for 5 hours under Ar. ^c $[I] = 0.24 mmol L^{-1}$, $[rac-LA] = 4.8 mM$, reaction left at 25 °C for 24 hours under Ar. ^d After 24 h at 25 °C, the reaction was quenched by bubbling air through the system and the sample analysed. ^e Diffusion constants taken from the middle of the contour plot mapped using a peak heights fit method. ^f Estimated from the calculated hydrodynamic radii of the diffusing species.^{42,43} ^g Calculated as: $[rac-LA]_0/[I]_0 \times M_r(LA) \times \text{conversion}/100 + M_r(I)$, where $M_r(I) = 1236.5 g mol^{-1}$ and the conversion is taken from integration of the methine region of the 1H NMR spectrum (*rac*-LA, $\delta = 4.98-5.08$ ppm; PLA, $\delta = 5.09-5.24$ ppm). ^h Calculated considering $M_r(I) = M_r(HOiPr)$. ⁱ Determined by SEC in THF using triple detection methods.

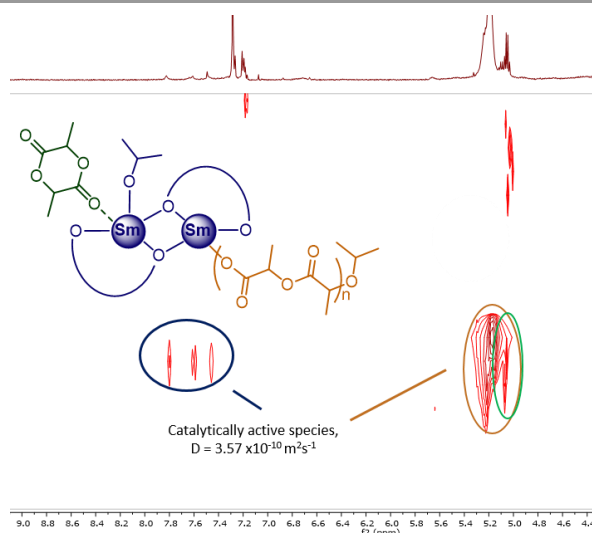
**Figure 3** 1H DOSY NMR spectrum of the reaction between $[(L^{Me}Sm(OiPr))_2]$ (0.24 mmol L^{-1}) and of *rac*-LA (20 equivalents, 4.8 mmol L^{-1}), 25 °C, 5 hours, $CDCl_3$ (1 mL) (corresponding to Table 3, entry 4).

Table 4 Selected polymerisation data for the polymerisation of *rac*-lactide with bis-alkoxide Ln complexes.^a

Entry	Solvent	Temp. (°C)	Initiator (I)	[<i>rac</i> -LA] ₀ : [Ln]	Time (min)	Conversion (%) ^b	Theo. <i>M</i> _n ^c kg mol ⁻¹	SEC <i>M</i> _n ^d kg mol ⁻¹	<i>Đ</i> ^d
1	Dichloromethane	25	[{L ^t BuNd(O <i>i</i> Pr)} ₂]	500	60	96	68.5	117.2	1.38
2	Dichloromethane	25	[{L ^t BuNd(O <i>i</i> Pr)} ₂]	1000	60	95	136.9	247.2	1.05
3	Dichloromethane	25	[{L ^{Me} Sm(O <i>i</i> Pr)} ₂]	150	120	40	8.7	5.8	1.03
4	Dichloromethane	25	[{L ^{Me} Yb(O <i>i</i> Pr)} ₂]	150	120	4	-	-	-
5	Toluene	80	[{L ^t BuNd(O <i>i</i> Pr)} ₂]	500	5	96	68.5	208.3	1.36
6	Toluene	80	[{L ^t BuNd(O <i>i</i> Pr)} ₂]	1500	5	95	205.3	156.3	1.30
7	Toluene	80	[{L ^t BuNd(O <i>i</i> Pr)} ₂]	3000	5	96	410.5	370.8	1.10
8	Toluene	80	[{L ^{Me} Sm(O <i>i</i> Pr)} ₂]	500	5	96	69.1	350.0	1.36
9	Toluene	80	[{L ^{Me} Sm(O <i>i</i> Pr)} ₂]	1500	10	96	207.4	169.4	1.23
10	Toluene	80	[{L ^{Me} Yb(O <i>i</i> Pr)} ₂]	1500	10	80	173.0	101.3	1.07
11 ^e	-	130	[{L ^t BuNd(O <i>i</i> Pr)} ₂]	900	5	95	123.1	122.1	1.05
12 ^e	-	130	[{L ^{Me} Sm(O <i>i</i> Pr)} ₂]	900	5	74	96.0	136.4	1.45
13 ^e	-	130	[{L ^{Me} Yb(O <i>i</i> Pr)} ₂]	900	5	91	118.1	128.8	1.24

^a For polymerisation reactions in solvent, [*rac*-LA]₀ = 0.69 mol L⁻¹. ^b Conversion is taken from integration of the methine region of the ¹H NMR spectrum of aliquots of the crude reaction mixture (*rac*-LA, δ = 4.98–5.08 ppm; PLA, δ = 5.09–5.24 ppm). ^c Calculated as: ([*rac*-LA]₀/[Ln] × *M*_r(*rac*-LA) × conversion/100) + *M*_r(O*i*Pr + H). ^d Determined by SEC in THF using triple detection methods; *Đ* = *M*_w/*M*_n. ^e Carried out under melt conditions using molten lactide as the solvent.

Complex activity in the polymerisation of lactide

Complexes [{L^{Me}Sm(O*i*Pr)}₂], [{L^{Me}Yb(O*i*Pr)}₂] and [{L^tBuNd(O*i*Pr)}₂] were tested for the ROP of *rac*-LA under various conditions, both in solution and in melted monomer (Table 4).

In CH₂Cl₂ at 25 °C (Table 4, entries 1–4), poor to good activity was observed, with a slight heterotactic preference, regardless of the coordination motif (*P*_r 0.5–0.6). Terminal alkoxide complexes [{L^{Me}Sm(O*i*Pr)}₂] and [{L^{Me}Yb(O*i*Pr)}₂] showed significantly lower activity than bridging alkoxide complex [{L^tBuNd(O*i*Pr)}₂]. In agreement with insight provided by DOSY NMR, molecular weights obtained are double those expected if both alkoxide were initiating polymerisation, indicative of only one polymer chain growing from the dimer. The kinetics of ROP using [{L^tBuNd(O*i*Pr)}₂] were investigated (Figure S13) and showed a pseudo-first order behaviour in monomer concentration, with *k*_{obs} of 1.7 × 10⁻³ s⁻¹ (CDCl₃, 25 °C, [LA] = 0.69 mol L⁻¹, [*rac*-LA]₀: [Nd] = 150). For reference some of the most active systems at 25 °C from the literature include an yttrium phosphosalen based initiator developed by Williams and coworkers, which has a *k*_{obs} of 8.0 × 10⁻² s⁻¹ (THF, 25 °C, [LA] = 1 mol L⁻¹, [*rac*-LA]₀: [Y] = 1000).^{46,47}

In toluene at 80 °C (Table 4, entries 5–10), all complexes were extremely active, achieving near quantitative conversions between 5–10 minutes for ratio [*rac*-LA]₀: [Ln] superior to 500. Generally, bridging isopropoxide complex [{L^tBuNd(O*i*Pr)}₂] displayed better control of molecular weight than bridging phenoxide ligand complexes [{L^{Me}Ln(O*i*Pr)}₂] (Ln = Sm, Yb).

[{L^tBuNd(O*i*Pr)}₂] exhibited remarkable activity and control. In particular, when used at 166 ppm level ([*rac*-LA]₀: [Ln] of 3000, see Table 4 entry 7), polymers with *M*_n 370,000 g mol⁻¹ and dispersity (*Đ*) of 1.10 could be obtained. The linear relationship between *rac*-LA conversion and *M*_n at [*rac*-LA]₀: [Ln] of 1500 (Figure S18) was indicative of a well-controlled polymerisation, despite a steady rise in dispersities (*Đ*, reaching 1.41 after 10 mins, likely due to undesired transesterifications). Beyond this, *Đ* did not drastically increase even after a further 30 minutes stirring, suggesting catalyst deactivation. The kinetics of ROP using [{L^tBuNd(O*i*Pr)}₂] were also investigated at [*rac*-LA]₀: [Ln] of 1500 (Figure S16) and showed a pseudo-first order behaviour in monomer concentration, with *k*_{obs} of 7.5 × 10⁻³ s⁻¹, a rate which is faster than the bis(phenolate) N-heterocyclic carbene Nd/Li system developed by Ni *et al* (*k*_{obs} = 1.21 × 10⁻³ s⁻¹), tested under analogous conditions (toluene, 70 °C, [L-LA] = 1 mol L⁻¹, [L-LA]₀: [Nd] = 1000).⁴⁸ Unfortunately, for all complexes, no tacticity bias could be observed under these conditions (*P*_r = 0.5). No significant trend in terms of rate could be identified across the different lanthanides either. It is worth noting that SEC *M*_n values are in agreement with those expected based on the [*rac*-LA]₀: [Ln] ratio, so that at 80 °C in toluene, every isopropoxide group of [{LLn(O*i*Pr)}₂] likely initiates polymerisation. Attempts to follow the polymerisation at 80 °C in toluene-*d*₈ by DOSY proved difficult so that further mechanistic consideration would be speculative.

Whilst not common within the rare-earth field, polymerisation reactions under industrially relevant conditions of monomer melt at 130 °C were undertaken (Table 4, entries 11–13).^{49,50} The gel point was achieved for all complexes within 5 minutes, which, in some cases hindered conversion due to mass-transfer limitations. Despite this, experimental molecular weights showed a good fit to the calculated values, assuming all isopropoxide groups initiated polymerisation, with especially good control for $[\{L^{tBu}Nd(OiPr)\}_2]$ (M_n 122,000 g mol⁻¹, \bar{D} 1.05).

The products of hydrolytic degradation $[L^{tBu}_2Sm_2(OiPr)(OH)]$ and $[L^{tBu}_2Yb_2(OiPr)(OH)]$ were also tested in the ROP of *rac*-LA and showed comparable activity to bis-alkoxide species, albeit with less control (see ESI, Tables S1–S3). This is likely due to the –OH group being slow polymerisation initiators, in addition to leading to carboxylic-acid terminated polymer chains, which could act as chain termination or chain transfer agents.

Conclusion

In conclusion, four new dimeric lanthanide alkoxide complexes with bipyrrrolidine salan ligands have been prepared, and complexes has been characterised via single-crystal X-ray diffraction and elemental analysis. Various coordination motifs were seen depending on the ligand and the metal used. Hydrolytic degradation of these complexes allowed the preparation of three dimeric mixed alkoxide/hydroxide and bis-hydroxide products. $[\{L^{tBu}Nd(OiPr)\}_2]$ proved very active for the controlled ring-opening polymerisation (ROP) of *rac*-lactide (LA), in melt monomer and in solution, yielding high molecular weight polymer (up to 370,000 g mol⁻¹) in a predictable and controlled fashion. In particular, under industrially relevant conditions (130 °C in melt monomer), PLA with M_n 122,000 g mol⁻¹ (\bar{D} 1.05) could be achieved in 5 minutes. ¹H DOSY NMR spectroscopy was employed to investigate the nature of the catalytic active species, which proved to be dinuclear.

Experimental section

Materials and methods

All metal complexes were synthesised under anhydrous conditions, using MBraun gloveboxes and standard Schlenk techniques. All chemicals used were purchased from Strem and Sigma-Aldrich and used as received unless stated otherwise. Dry solvents were obtained from MBraun solvent purification system and stored under nitrogen over 3 Å molecular sieves. CDCl₃ was dried over CaH₂, distilled prior to use, and stored under nitrogen. *rac*-LA was recrystallised twice from dry toluene and stored under nitrogen. Ligands L^{Me} and L^{tBu} were synthesised following literature procedures.²⁵ NMR spectra were recorded using a Bruker Avance III 500 MHz spectrometer. Coupling constants are given in Hertz. DOSY NMR experiments were carried out at concentration of 10 mg mL⁻¹ of monomer in 1 mL deuterated CDCl₃ (see details in ESI) and processed using MestReNova software (v10). Diffusion coefficients were determined by comparison against solvent diffusion signals and compared to those recorded in the literature.⁴³ Elemental

analysis was determined by Stephen Boyer at London Metropolitan University. SEC was performed using two PL MIXED.D 300 × 7.5 mm columns in series, with THF as the eluent, at a flow rate of 1 mL min⁻¹ on a Agilent 1260 GPC/SEC MDS instrument at 35 °C. The polymer samples were dissolved in SEC grade THF and filtered prior to analysis. Molecular weights were determined using triple detection methods (differential refractive index detector (calibrated using polystyrene standards), a viscometer detector and a light scattering detector (90°, with a calculated dn/dc range = 0.095–0.11 mLg⁻¹, as calculated from the RI). MALDI-ToF spectrometry analysis was carried out on a Bruker Autoflex speed instrument in reflector positive mode, using DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix at a concentration of 10 mg mL⁻¹ in THF, with added sodium trifluoroacetate (see ESI). All X-ray diffraction data was obtained at 150 K, on a Rigaku SuperNova or Excalibur diffractometer using Cu-Kα or Mo-Kα radiation (λ = 1.54184 Å or 0.71073 Å). Structures were using the SHELXL-2014 suite of programs.

Complex synthetic procedure

In a typical experiment, ligand L^{tBu} (576 mg, 1.0 mmol,) was dissolved in toluene (5 mL) then added to a stirred solution of $[Nd(OiPr)_3]$ (1.0 mmol) in toluene (10 mL). The solution was then heated to 60 °C and left to stir for 3 hours. After this time the solvent was removed and the solid was dissolved in the minimum quantity of dry hexane/toluene and recrystallised at -20 °C. The resultant crystalline solid was washed with cold dry hexane (3 × 1 mL) then dried, to yield the product as a solid, stored under an argon atmosphere.

$[\{L^{tBu}Nd(OiPr)\}_2]$. Blue powder (680 mg, 86% yield). Elemental (CHN) Analysis; (Calculated: C₈₂H₁₃₀N₄O₆Nd₂) C 63.2%, H: 8.42%, N: 3.60%, (Experimental) C: 62.74%, H: 8.16%, N: 3.62%.

$[\{L^{tBu}Sm(OiPr)\}_2]$. White powder (55 mg, 7% yield). (Elemental (CHN) Analysis; (Calculated: C₈₂H₁₃₀N₄O₆Sm₂) C: 62.79%, H: 8.35%, N: 3.57%, (Experimental) C: 63.41%, H: 8.79%, N: 3.61%.

$[\{L^{Me}Sm(OiPr)\}_2]$. White powder (310 mg, 51% yield). ¹H NMR (500 MHz, CDCl₃, δ_H , ppm); 7.92 (2H, ArH), 7.43 (2H, ArH), 6.90 (2H, ArH), 6.25 (2H, d, J = 12.5 Hz, CHH), 6.18 (2H, OCH(CH₃)₂), 6.01 (6H, CH₃), 5.21 (2H, CHH), 4.8 (2H, ArH), 2.83 (2H, d, J = 12.5 Hz, CHH), 2.50 (6H, CH₃), 2.05 – 2.32 (12H, OCH(CH₃)₂), 2.00 (6H, CH₃), 1.88 (2H, CHH), 0.72 (4H, CH₂), 0.2 (6H, CH₃), -0.04 (2H, CH), -0.33 (2H, CH), -0.33 (2H, CH), -0.69 (4H, CH₂), -1.02 (4H, CH₂), -1.53 (2H, CH), -2.45 (2H, CH), -2.70 (2H, CH), -4.07 (2H, CH), -4.56 (2H, CH). 2D DOSY (500 MHz, CDCl₃, D_{sol} = 1.77 × 10⁻⁹ m²s⁻¹, 298 K), 5.89 × 10⁻¹⁰ m²s⁻¹. Elemental (CHN) Analysis; (Calculated: C₅₈H₈₂N₄O₆Sm₂) C: 56.54%, H: 6.71%, N: 4.55%, (Experimental) C: 56.70%, H: 6.81%, N: 4.46%.

$[\{L^{Me}Yb(OiPr)\}_2]$. White powder (298 mg, 47% yield). Elemental (CHN) Analysis; (Calculated: C₅₈H₈₂N₄O₆Yb₂) C: 54.53%, H: 6.47%, N: 4.39%, (Experimental) C: 54.16%, H: 6.59%, N: 4.34%.

Isolation of degradation products could be achieved from recrystallisation of the filtrate from the precipitation of the analogous bis-alkoxide complex. Washing with the cold hexane (3 x 10 mL) and drying under vacuum yielding a crystalline material which could be characterised by CHN analysis and single crystal X-ray diffraction. Hydrolysis reactions monitored by ^1H NMR as in the case of $[\{\text{L}^{\text{Me}}\text{Yb}(\text{O}i\text{Pr})\}_2]$ and $[\{\text{L}^{\text{Me}}\text{Sm}(\text{O}i\text{Pr})\}_2]$ were carried out by exposing a J-Young tube solution of lanthanide sample in CDCl_3 to a flow of compressed air for 30 mins. The vessel was sealed and monitored via ^1H NMR spectroscopy

$[\text{L}^{\text{tBu}}_2\text{Sm}_2(\text{O}i\text{Pr})(\text{OH})]$. Cream powder (530 mg, 69% yield) (Elemental (CHN) Analysis; (Calculated: $\text{C}_{79}\text{H}_{124}\text{N}_4\text{O}_6\text{Sm}_2$) C: 62.16%, H: 8.19%, N: 3.67%, (Experimental) C: 61.66%, H: 8.15%, N: 3.68%.

$[\text{L}^{\text{tBu}}_2\text{Yb}_2(\text{O}i\text{Pr})(\text{OH})]$. White powder (298 mg, 47% yield). Elemental (CHN) Analysis; (Calculated: $\text{C}_{79}\text{H}_{124}\text{N}_4\text{O}_6\text{Yb}_2$) C: 54.53%, H: 6.47%, N: 4.39%, (Experimental) C: 54.16%, H: 6.59%, N: 4.34%.

$[\{\text{L}^{\text{tBu}}\text{Sm}(\text{OH})\}_2]$. White powder (90 mg, 18% yield) ^1H NMR (500 MHz, CDCl_3 , δ_{H} , ppm); 22.36 (1H, SmOH), 8.28 (2H, ArH), 8.05 (2H, ArH), 6.63 (2H, CHH), 3.14 (4H, NCH_2), 2.87 (2H, CHH), 1.93 (18H, $\text{C}(\text{CH}_3)_3$), 0.54 (18H, $\text{C}(\text{CH}_3)_3$), -0.85 (2H, CH_2), -2.04 (2H, CH_2), -3.02 (2H, CH_2), -4.48 (2H, CH_2), -7.22 (2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , δ_{C} , ppm); 172.4 (C-O), 137.1 (Ar), 135.7 (Ar), 128.4 (Ar), 127.8 (Ar), 126.0 (Ar), 66.6 (NCH), 59.6 (NCH₂), 52.8 (NCH₂), 36.0 ($\text{C}(\text{CH}_3)_3$), 35.2 ($\text{C}(\text{CH}_3)_3$), 32.6 ($\text{C}(\text{CH}_3)_3$), 29.6 ($\text{C}(\text{CH}_3)_3$), 22.8 (CH_2), 18.7 (CH_2), 16.8 (CH_2), 14.3 (CH_2). 2D DOSY (500 MHz, CDCl_3 , $D_{\text{sol}} = 2.09 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, 298 K), $4.69 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Elemental (CHN) Analysis, (Calculated: $\text{C}_{76}\text{H}_{118}\text{N}_4\text{O}_6\text{Sm}_2$) C: 61.49 %, H: 8.01 %, N 3.77 %, (Experimental) C: 60.96 %, H 7.77 %, N 3.74 %.

Polymerisation of lactide

Polymerisation in solution. In a typical experiment, *rac*-lactide (1.0 g, 6.9×10^{-3} mol) was added to an ampule with a J-Young cap in 10 mL of solvent, with initiator (6.9×10^{-6} mol). If toluene was the chosen solvent, the polymerisation ran at 80 °C for the chosen time, whereas polymerisations in CH_2Cl_2 were carried out at 25 °C. Once complete the solvent was immediately removed *in vacuo* and the crude product analysed via ^1H NMR. The polymer was then washed with methanol (3 x 10 mL) and dried under high vacuum prior to GPC analysis.

Polymerisation in monomer melt. In a typical experiment, *rac*-lactide (1.0 g, 6.9×10^{-3} mol) was added to an ampule with a J-Young cap with initiator (7.7×10^{-6} mol) and placed into an oil bath set at 130 °C. Upon solidification of the mixture, the vial was exposed to air and approximately 5 mL of reagent grade CH_2Cl_2 was added to terminate the polymerisation. Removal of the solvent *in vacuo* yielded the crude product which was analysed via ^1H NMR spectroscopy. The polymer was then washed with methanol (3 x 10 mL) and dried under high vacuum.

In-situ monitoring of polymerisation kinetics. In a typical experiment, *rac*-lactide (60 mg, 4.16×10^{-4} mol) was added to an NMR tube with a J-Young cap in 0.6 mL of tol-d_8 , with metal

complex initiator (1.38×10^{-6} mol). The tube was allowed to equilibrate at 80 °C for 5 minutes, the magnetic field was homogenised and experiments were ran 5 minutes until completion. Quenching of the reaction was carried out by bubbling compressed air with a needle through the solvent for 5 minutes.

Conflicts of interest

There are no conflicts to declare.

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